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Institute of Mathematical Sciences
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The Cooling of a Gas by Radiation

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THE COOLING OF A GAS BY RADIATION

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ABSTRACT

We consider a gas composed of atoms having two electronic states. Transitions between these two states can take place by collisions, and by emission or absorption of radiation. When the radiative transition probabilities are small compared with those due to collisions, a " temperature" may be defined for the translational motion. We formulate the general problem for the case where the total concentration of the gas depends on the space co-ordinates in a given way, and the possibility of the " imprisonment" of the radiation emitted is taken into account. In this case the problem leads to a pair of coupled integro-differential equations, from which the " temperature" and the concentration of atoms in the excited state are obtained as functions of space and time. Neglecting the resonance radiation and the spatial variation of the temperature, we have made calculations for the case when the energy difference between the two states is of the order kT, for a number of values of the ratio between radiative and collisional transition probabilities. The results are applied to the problem of the cooling of the atmospheric gas at high altitudes (100 Km) at night, as a result of the magnetic dipole transitions between the components of the ^3P state of the oxygen atom.

TABLE OF CONTENTS

Page

1. Introduction 1
2. Formulation of the General Problem. 3
    - 2.1 Collisional Transitions 4
    - 2.2 The Escape of Energy by Radiation 7
    - 2.3 Energy Balance and the " temperature" T 9
3. Solution of a Simplified Problem 10
    - 3.1 Solution of the System (35)-(37) 12
4. Application to the Upper Atmosphere 15

Appendix 20

1. Introduction

In a recent paper, Bates[1] suggested that magnetic dipole transitions between the components of the ^3P state of the oxygen atom could lead to a significant cooling of the upper atmosphere in that region where oxygen atoms are abundant, i.e., about 100 Km above the earth. The (inverted) triplet state in question has splittings of the order of .02 e.v., which are of the order of the gas kinetic energy at these altitudes, so that the number of atoms in excited states of the triplet will be large; and thus, while the transition probabilities of the $^3P_0 - {}^3P_1$, $^3P_1 - {}^3P_2$ transitions are small ($10^{-5} - 10^{-4} \mathrm{sec}^{-1}$; see Pasternack[2]), yet the total number of transitions per unit volume per second may be large and so may be the total energy transferred in this way.

These considerations are limited by the assumption of a Boltzmann distribution, which is valid only for a system in thermodynamic equilibrium, and by the neglect of the possibility that the radiation emitted will be absorbed by other atoms, leading to the familiar problem of the " imprisonment of resonance radiation" . The purpose of the present work is first, to formulate the problem of the cooling of a gas by the emission of radiation without assuming the Boltzmann distribution for the atoms in various states and without neglecting the effect of imprisonment of the radiation, and second to carry out numerical calculations appropriate for application to the upper atmosphere when the effect of imprisonment of the radiation is neglected as a first approximation.

To simplify the calculations, we shall consider a gas composed of atoms having two electronic states 1 and 2 , and distributed in space in a given manner (such as the gas in the atmosphere). Transitions between these two states can take place by collisions and by emission or absorption of radiation. In a collisional transition, energy is transferred between the translational and electronic modes of the atom; in a radiative transition an atom may emit a quantum $h\nu_{21}$ of radiation, or it may absorb a quantum $h\nu_{21}$ that has been emitted by another atom in the gas. We shall assume that there is no incident radiation from an external source having a frequency ν_{21} , so that the radiation energy of this frequency comes only from quanta emitted by atoms in the system. These quanta will eventually be lost to the system after undergoing a series of absorptions and re-emissions by other atoms in traversing the gas. The problem now is to study the change of state of the system, starting with suitable initial conditions. At time $t = 0$ our gas is in statistical equilibrium at a given temperature T_0 as a result of collisions alone. Then, for $t > 0$, we " switch on" the radiative transitions, so that there is a net loss of energy from the system for $t > 0$, and we now ask the following question: at what rate is energy lost from the system?

The behavior of the system obviously depends on the spatial distribution of the atoms, and on the values of the collisional and radiative cross-sections. Let the average cross-section for gas kinetic collisions be σ_0, and let those for excitation and de-excitation of the state 2 by collisions be σ_{12} and σ_{21} , respectively, and let the Einstein A coefficient for the 2 - 1 transition be A_{21} . Let the total number density of the gas be N and the average velocity of the atoms be v . In the extreme case where

$$A_{21} \gg N.v.\ \sigma_{21} \qquad (1)$$

the excited atoms in state 2 are removed by emission of radiation as soon as they are excited by collisions. The rate of loss of energy of the system is governed by the rate of collisional excitation (which is a function of time), and by the effect of the " imprisonment" of the radiation in the gas. In this case, the distribution of the atoms in the two states 1 and 2 , which varies with time, will not be given by the Boltzmann theorem at all since the departure from thermodynamic equilibrium is so great that it is not meaningful to speak of a " temperature" . In the other extreme, where

$$A_{21} \ll N.v.\,\sigma_{21} \quad , \qquad (2)$$

the rate of loss of energy by radiation is so small that one may regard the system as undergoing a continuous transition through states which differ only slightly from the equilibrium state.

These extreme cases can be treated easily, but are not general enough for our purpose. In the present work we shall consider the case where

$$A_{21} \ll N.v.\,\sigma_o \quad , \qquad (3)$$

which is less stringent than (2), since in general $\sigma_o > \sigma_{21}$, and usually $\sigma_o \gg \sigma_{21}$. Under the condition (3), the frequency of elastic collisions is high compared with that of emission of radiation, so that the atoms make enough collisions to redistribute their kinetic energy of translation between radiative transitions. In this case, it is possible to assume that while the distribution of the atoms in the two electronic states 1 and 2 may deviate greatly from the Boltzmann distribution, yet the translational degrees of freedom may be characterized by a " temperature" T , defined by the kinetic energy of the atoms. On this assumption, the problem will be to find the " temperature" T and the ratio N_2/N_1 of the numbers of atoms in the two states 2 and 1 as functions of time and space for certain initial and boundary conditions.

2. Formulation of the general problem

We consider a gas species of number density $N = N(\underline{r})$ that has two states, a ground state 1 and an excited state 2 , of densities $N_i(\underline{r}\,,\,t)$, (i = 1, 2):

$$N(\underline{r}) = N_1(\underline{r},\,t) + N_2(\underline{r}\,,\,t) \quad . \qquad (4)$$

We shall define an effective temperature $T = T(\underline{r}, t)$ in terms of the total kinetic energy per unit volume. It is convenient to deal with the case when there are other gas atoms present in addition to the gas species we are concerned with primarily; these other atoms enter into the thermal collisions, but do not participate in any way in the radiative processes. (In the problem under consideration, there would be nitrogen molecules present as well as oxygen atoms). Accordingly, the total number density of all particles will be $X(\underline{r})$, which may be greater than $N(\underline{r})$. Thus the total kinetic energy per unit volume is

$$(3/2)kTX \tag{5}$$

which serves to define the effective temperature T.

Let the collisional cross-sections for the excitation and de-excitation of the state 2 be $\sigma_{12}(v)$ and $\sigma_{21}(v)$, where v is the relative velocity of the colliding particles. There will also be radiative effects specified by the rates $B_{12}\,\rho(\nu_{12};\,\underline{r},t)$ and $\left\{A_{21} + B_{21}\rho(\nu_{21};\,\underline{r},t)\right\}$, where A, B are Einstein coefficients and ρ is the radiation energy density.

2.1 Collisional transitions

In a state of equilibrium determined by collisional processes alone, we have

$$N_i = N_i^o(\underline{r}) \text{ only}, \quad T = T^o(\underline{r}) \text{ only}, \tag{6}$$

and

$$N_2^o(\underline{r})/N_1^o(\underline{r}) = (g_2/g_1) \quad \exp\left\{-\ \varepsilon_{21}/kT^o(\underline{r})\right\} \qquad \text{(u)}$$

where the level splitting ε_{21} is given by

$$\varepsilon_{21} = \frac{1}{2} M_R\, v_o^{\,2} = h\nu_{21} \;. \tag{8}$$

M_R is the reduced mass of the colliding particles, and g_1, g_2 are the statistical weights of the states 1 and 2.

If X is the total number density of particles that may excite or de-excite our atom, the rate of increase of N_2 due to collisions is

$$\left(\frac{\partial}{\partial t} N_2 \right)_{\text{coll}} = N_1 X \int_{v_o}^{\infty} dv.v.f(v).\ \sigma_{12}(v) - N_2 X \int_{o}^{\infty} dv.v.f(v).\ \sigma_{21}(v), \qquad (9)$$

where f(v) is the velocity distribution function.

The two cross-sections σ_{12} , σ_{21} are not independent, but are related atomic properties. In particular, if we define two velocities v , v' , related by

$$v^2 = v'^2 + (2/M_R)\ \varepsilon_{21} = v'^2 + v_o^2 , \qquad (10)$$

then the ratio $\sigma_{12}(v)/\ \sigma_{21}(v')$ depends only on atomic properties such as v, v' , g , etc., and not on macroscopic quantities like the temperature. On account of this fact, we may calculate this ratio of cross-sections from the principle of detailed balance for conditions of statistical equilibrium, and be sure that the result will still hold when there is no statistical equilibrium.

The condition of detailed balance is

$$N_1\ \sigma_{12}\ (v).f(v).v.dv = N_2\ \sigma_{21}(v').f(v').v'.dv' \ , \qquad (11)$$

where the conditions (7), (10) must be satisfied. Equation (10) gives the result v.dv = v'.dv' . If we substitute a Maxwellian function for the velocity distribution function f(v):

$$f(v) = 4\pi\ (M_R/2\pi kT)^{3/2}\ .\ v^2\ .\ \exp \left\{ - M_R v^2/2kT \right\} , \qquad (12)$$

then equation (11) leads to the result

$$\sigma_{12}(v)/\ \sigma_{21}(v') = (g_2/g_1).\ \ (v'/v)^2 \tag{13}$$

Substituting (13) in (9), we get*, †

$$\left(\frac{\partial}{\partial t} N_2\right)_{coll} = X.F(T)\ \left\{ N - N_2\ \ \left(1 + \frac{g_1}{g_2}\ e^{\varepsilon_{21}/kT}\right)\right\}\ , \tag{14}$$

where

$$F(T) = \int_{v_o}^{\infty} dv.v.f(v).\ \sigma_{12}(v)\quad . \tag{15}$$

Neither the precise form nor even the numerical value of $\sigma_{12}(v)$ is known, but in view of the Boltzmann factor in $f(v)$ the precise form does not much matter as long as we can make a reasonable estimate of σ close to the threshold v_o . If we put

$$\sigma_{12}\ (v) = \begin{cases} 0\ , & v < v_o \\ \sigma\ , & v > v_o \end{cases} \tag{16}$$

then

$$F(T) = 2\sigma\ \left(\frac{2kT}{M_R\pi}\right)^{1/2} \exp\left[-\varepsilon_{21}/kT\right]\ \left(1 + \frac{\varepsilon_{21}}{kT}\right). \tag{17}$$

---

[*] It is clear that in equilibrium, substituting (7) in (14) yields $\left(\frac{\partial}{\partial t} N_2\right)_{coll} = 0$, as must be the case.

[†] In writing down equation (14), we assume the form (12) for $f(v)$, which implies equilibrium conditions. Since we have made the restriction (3) and have assumed the possibility of defining a temperature T in (5), the use of (12) in obtaining (14) is a consistent assumption.

2.2 The escape of energy by radiation*

The rate of decrease of $N_2(\underline{r},t)$ due to emission of the quantum $h\nu_{21}$ is

$$N_2(\underline{r},t) \left\{ A_{21} + B_{21} \ \rho\,(\nu_{21};\underline{r},t)\right\} = N_2(\underline{r},t) \ \gamma(\underline{r},t) \ , \qquad (18)$$

where ρ is the radiation energy density of frequency ν, measured per unit frequency range. Instead of calculating this rate by evaluating the density ρ due to the radiation emitted by other atoms in the system, we proceed as follows.

Let the absorption cross-section of radiation of frequency ν be k_ν so that the radiation intensities $I_o(\nu)$, $I_s(\nu)$, measured a distance s apart, are related by

$$I_s(\nu) = I_o(\nu).\exp(-k_\nu.N_1.s) \quad . \qquad (19)$$

k_ν is some function of frequency ν, the precise form depending on the mechanism responsible for the line shape. Let $P(\nu)$ be the intensity distribution of the spectral line, so normalized that

$$\int_{SL} d\,\nu.P(\nu) = 1, \qquad (20)$$

where " SL" indicates that the integration extends over the whole of the spectral line.

Now $\Gamma\,(\xi,t)$, the probability that a quantum of radiation traverses a distance $\xi = |\,\underline{r} - \underline{r}'\,|$ before being absorbed, is

---

* For the formulation of a similar but less general problem, see Holstein[3]

$$\Gamma(\xi,\ t) = \int_{SL} d\nu \,.\, P(\nu) .\ \exp\left\{ - k_\nu \int_0^\xi d\xi . N_1(\xi,\ t) \right\} . \tag{21}$$

The number of quanta emitted in the volume element $d^3\underline{r}'$, and directed into the solid angle dS/ξ^2, per second, is

$$\frac{dS}{4\pi\xi^2} \,.\, N_2(\underline{r}',t) .\ \gamma\,(\underline{r}',\ t).d^3\underline{r}' \quad , \tag{22}$$

and thus the number of quanta that are absorbed in the volume element $d^3\underline{\xi} = dS.d\xi$ is

$$-\frac{dS}{4\pi\xi^2} \,.\, N_2(\underline{r}',t) .\ \gamma\,(\underline{r}',\ t) .\ d^3\underline{r}' \,.\, \frac{\partial\Gamma(\xi,t)}{\partial\xi} \,.\, d\xi . \tag{23}$$

The number of quanta absorbed per unit volume element per second at $\underline{r}$ due to radiation coming from all space is

$$\frac{1}{d^3\underline{\xi}} \,.\, \int d^3\underline{r}' \ .\ \text{expression (23)} ,$$

which is

$$- (1/4\pi) \,.\, \int d^3\underline{r}' \,.\, N_2(\underline{r}',t) \,.\, \gamma\,(\underline{r}',t) .\ \frac{\partial\Gamma(\xi,t)}{\partial\xi} \ . \tag{24}$$

$G(\underline{r},\underline{r}';t)$, the probability that a quantum emitted at $\underline{r}'$ is absorbed in unit volume at $\underline{r}$, is given by

$$G(\underline{r},\underline{r}';t) = G(\underline{r}',\underline{r};t) = \frac{-1}{4\pi\xi^2} \,.\, \frac{\partial\Gamma(\xi,t)}{\partial\xi} \ . \tag{25}$$

Thus, from equations (18), (24), (25), the net rate of change of $N_2(\underline{r},t)$ due to radiative processes is

$$\left(\frac{\partial}{\partial t} N_2\right)_{rad} = -N_2(\underline{r},t)\,\gamma\,(\underline{r},t) + \int d^3\underline{r}'.N_2(\underline{r}',t).\gamma(\underline{r}',t).G(\underline{r},\underline{r}';t) \ , \tag{26}$$

and combining this with (14) we have the total rate of change of $N_2(\underline{r},t)$:

$$\frac{\partial}{\partial t} N_2 = X.F(T) \left[N - N_2 \left\{ 1 + (g_1/g_2).e^{\varepsilon_{21}/kT} \right\} \right] - N_2.\gamma(\underline{r},t) + \\ + \int d^3\underline{r}'.N_2(\underline{r}',t).\gamma(\underline{r}',t).G(\underline{r},\underline{r}';t) \qquad (27)$$

which is one of our fundamental equations.

This differential-integral equation can be simplified somewhat if we neglect the induced emission of radiation compared with the spontaneous emission, so that equation (18) gives

$$\gamma\ (\underline{r},t) = A_{21} = \text{constant.} \qquad (28)$$

This neglect is justified if there is no incident radiation from an external source, and if ρ arising from the atoms in the system is small. If we use (28), equation (27) becomes

$$N_2 = X.F(T) \left[N - N_2 \left\{ 1 + (g_1/g_2).e^{\varepsilon_{21}/kT} \right\} \right] - N_2.A_{21} + \\ + A_{21} \int d^3\underline{r}'.N_2(\underline{r}',t).G(\underline{r},\underline{r}';t) \quad . \qquad (29)$$

However, equation (29) still contains two unknown functions, $N_2(\underline{r},t)$ and $T(\underline{r},t)$, and thus to solve the problem we need another equation, which is furnished from the definition (5) of the effective temperature T .

2.3 Energy balance and the " temperature " T

The kinetic energy per unit volume of the gas is $(3/2)kTX$. This is changed only by collisions and not by radiative transitions, because the radiative processes by themselves change only N_2 and N_1 but do not change the kinetic energy. Hence, the variations of the temperature at any given position and time are determined by the condition

$$\frac{\partial}{\partial t}\left\{(3/2)kTX\right\} + \varepsilon_{21}\left(\frac{\partial}{\partial t} N_2\right)_{\text{coll}} = 0 \;,$$

and from the equation (14) this reduces to

$$\frac{\partial}{\partial t}\left\{(3/2)kTX\right\} + \varepsilon_{21}\; XF(T)\left[N - N_2\left\{1 + (g_1/g_2).e^{\varepsilon_{21}/kT}\right\}\right] = 0. \quad (30)$$

In equations (29), (30) we have two coupled non-linear integro-differential equations which, together with the appropriate boundary conditions, will specify the two functions $N_2(\underline{r},t)$ and $T(\underline{r},t)$.

3. Solution of a Simplified Problem

The solution of the two equations (29), (30) in their full generality presents considerable difficulties. In the present work, as a first approximation to the solution, we neglect the effect of imprisonment of resonance radiation by putting $G(\underline{r},\underline{r}',t) = 0$. It is clear that this will give an over-estimate of the rate of energy loss due to radiation for the present problem since in this case all quanta radiated are immediately lost, there being now no mechanism for retaining them within the system.

To reduce the complications still further, we take the total densities N , X as absolute constants, so that there is now no space dependence left in the problem. Thus, our basic equations obtained from (29) and (30) are

$$\frac{\partial}{\partial t} N_2 + \left[XF(T)\left\{1 + (g_1/g_2).e^{\varepsilon_{21}/kT}\right\} + A_{21}\right] N_2 = XNF(T), \quad (31)$$

$$\frac{\partial}{\partial t}\left\{(3/2)kTX\right\} + \varepsilon_{21}\; XF(T)\left[N - N_2\left\{1 + (g_1/g_2).e^{\varepsilon_{21}/kT}\right\}\right] = 0, \quad (32)$$

where now N_2 and T are functions of time only, and all other quantities (X, N, g_1, g_2, ε_{21}, A_{21}) are constants.

We now wish to solve the problem of equations (31) and (32) for $t > 0$ with the following initial conditions*

$$T = T_o \ , \ \partial T/\partial t = 0, \text{ at } t = 0 \tag{33}$$

In order to solve the problem of (31) - (33), we introduce the following dimensionless variables and constants:

$$\begin{aligned} n &= N_2/N \\ x &= \varepsilon_{21}/kT \\ \tau &= c_o t \\ XF(T) &= c_o . \phi(x) \\ g &= g_1/g_2 \\ \mu &= 2N/3X \\ \lambda &= A_{21}/c_o \end{aligned} \tag{34}$$

where c_o is a constant of the order of the reciprocal of the time between two excitational collisions.

In this new notation, the problem is

$$\frac{\partial n}{\partial \tau} + \left[\lambda + \phi(x).(1 + g.e^x) \right] n = \phi(x) \tag{35}$$

$$\frac{\partial}{\partial \tau} (1/x) + \mu \, \phi(x) \left[1 - n.(1 + g.e^x) \right] = 0 \tag{36}$$

to be solved for $\tau > 0$ with the initial conditions

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* Substituting (33) in (31) and (32), we find that at $t = 0$, we have $N_2 = N_2^o$ of equation (7), and also $\partial N_2/\partial t = - A_{21} N_2$. Both these results are eminently reasonable, and show that the initial conditions (33) are satisfactory for describing how radiative 2-1 transitions disturb the initial statistical equilibrium.

$$x = x_o, \quad \partial x/\partial t = 0, \qquad \text{at } \tau = 0. \tag{37}$$

We shall take

$$\phi(x) \simeq e^{-x} \tag{38}$$

as an approximation, bearing in mind that while the precise form of F(T) is not known, yet an approximation such as (38) does yield the basic, exponential, T-dependence of equation (17).

3.1 Solution of the system (35) - (37)

A standard way of solving two coupled equations is to eliminate one of the two dependent variables: here it is clearly convenient to eliminate n rather that x. If we carry out the elimination, we get

$$\left[1 + \frac{(\partial/\partial\tau)(1/x)}{\mu\phi(x)}\right] \frac{1}{1+g.e^{x}} = n \tag{36'}$$

and

$$\frac{d^2x}{d\tau^2} + \left(\frac{dx}{d\tau}\right)^2 \left\{-\frac{2}{x} + \frac{1}{1+g.e^{x}}\right\} + \frac{dx}{d\tau}\ \lambda + g + e^{-x} + \frac{\mu g x^2}{1+ge^{x}} - \lambda u x^2 e^{-x} = 0. \tag{39}$$

Thus the problem is reduced to the solution of the equation (39) with the initial conditions (37). The independent variable τ only appears as $d/d\tau$, so that it is clearly convenient to transform (39) so as to make $dx/d\tau$ (or some function of it) the dependent, and x the independent variable; and in particular, because the coefficient of $(dx/d\tau)^2$ in (39) differs from $-(2/x)$ by a small quantity (namely $1/(1+g.e^{x})$), we introduce the new dependent variable

$$y = y(x) = \frac{1}{x^2} \cdot \frac{dx}{d\tau} \quad . \tag{40}$$

When y is substituted into (39) the latter will have a y^2-term of the form

$y^2/(1+g.e^x)$. Since this term is small, we may neglect it* and discuss the solution of

$$y \,.\, dy/dx \;+\; y \,.\, J(x) - K(x) = 0$$

$$x^2.J(x) = \lambda + g + e^{-x} + \frac{\mu g.x^2}{1 + g.e^x} \;;\; x^2.K(x) = \lambda\mu e^{-x} \qquad (41)$$

with the initial condition

$$y = 0 \quad \text{at} \quad x = x_o . \qquad (42)$$

This equation (41) has been integrated numerically for the following values of the parameters:†

$$x_o = \frac{1}{2} , \quad g = 2 , \quad \mu = \frac{1}{4} ,$$
$$\lambda = 1 , \; 10^{-3} , \; 10^{-5} , \; 10^{-7} . \qquad (43)$$

---

[*] Calculations have been made and they show that the neglect of the y^2-term does not produce any significant changes, either in the general character of the solution or in its numerical values, for the range of parameters used here.

[†] For the theory and the calculation to be valid, the condition (3) must be satisfied. As λ in (34) is

$$\lambda = \frac{A}{X \int \sigma_{12} \, v \, f(v) \, dv} ,$$

the condition (3) in terms of λ becomes

$$\lambda \ll \frac{\sigma_o}{\sigma_{12}} .$$

While the value $\lambda \simeq 1$ is still permissible if $\sigma_o \gg \sigma_{12}$, the case $\lambda = 1$ and $\sigma = 10^{-16}$ cm^2 in Table 1 does not very well satisfy the above condition, and is hence included in parentheses in Table 1 only for comparison.

A detailed discussion of the solution of equation (41) is given in the Appendix: y rises very sharply just above x_o (in fact, dy/dx is ∞ at $x - x_o$) to a maximum at x_1, and then falls off to zero as x tends to infinity; beyond the maximum y(x) may be approximated by $\eta(x)$, defined as

$$\eta(x) = K(x)/J(x). \qquad (44)$$

Once we have y as a function of x, we can find $\tau(x)$ from equation (40), as $\int_{x_o}^{x} dx/ \; x^2.y(x)$, and then inversion gives $x = x(\tau)$. A transformation now gives the temperature T as a function of time t. Fig. 1 gives T(t) for $T(0) = 300^\circ K$, $\sigma = 10^{-16}$ cm^2 and a number of values of the Einstein coefficient A_{21}. Table 1 gives T (10 hours) for $T(0) = 300^\circ K$ and various values of σ and A_{21}.

It is of interest and importance to see the extent to which the ratio N_2/N_1 of the concentration of the two states deviates from the Boltzmann expression (7) for equilibrium distribution. If as in (6) we again denote the equilibrium value by a superscript o, we have from (34)

$$\frac{N_2(t)}{N_2{}^o(t)} = \frac{n(x)}{n^o(x)}$$

and from (7), $n^o(x) = 1/(1 + g\, e^x)$. Hence, from (35)

$$\frac{N_2(t)}{N_2{}^o(t)} = 1 - y(x)\; e^x/\mu \;,$$

$$\simeq 1 - \eta(x)\; e^x/\mu = (g + e^{-x})/(\lambda + g + e^{-x}) \qquad (45)$$

for $x > x_1$. Asymptotically, for large x (i.e., t),

$$N_2/N_2{}^o \rightarrow g/(\lambda + g) \quad . \qquad (45')$$

Thus it is seen that there will be appreciable deviation from the Boltzmann distribution if λ is not too small compared with g . Fig. 2 gives the ratio $N_2(t)/N_2^o(t)$ for $g = 2$ and various values of A_{21} , σ for which λ has the same value 1 .

4. Application to the Upper Atmosphere

We shall apply the calculations of the preceding section for the simplified model to those regions of the upper atmosphere where there are oxygen atoms. Here we have a triplet state $^3P_{0,1,2}$ with the following energy difference and transition probabilities (Pasternack)[2]:

$$^3P_o \text{ --- } {^3P_1} \qquad \nu = 68 \text{ cm}^{-1} \qquad A = 1.68 \times 10^{-5}/\text{sec} .$$

$$^3P_1 \text{ --- } {^3P_2} \qquad \nu = 158.5 \text{ cm}^{-1} \qquad A = 8.8 \times 10^{-5}/\text{sec} .$$

If we consider the transition $^3P_1$ --- $^3P_2$ alone, and for that region of the atmosphere where the total particle density X is $\sim 3.10^{13}$ cm^{-3}, (corresponding to an altitude of about 100 km), the appropriate values of the parameters are $g = 5/3$, $\mu \approx 1/4$, $x_o = 0.77$, which are comparable with those in (43). The value of the collisional cross-section σ of equation (16) is not known, and accordingly calculations have been carried out for three values of σ , namely 10^{-16}, 10^{-18}, 10^{-20} cm^2 . The value 10^{-18} cm^2 may perhaps be a plausible one; corresponding to it, the value of c_o of (34) is $\sim 4 \times 10^2$ sec. We are primarily interested in the cooling of the gas over night, so that we want to see how the temperature changes in a time $\sim$ 10 hours. From the results in Table I, it is seen that the fall in temperature is about 30 degrees. Thus, at this altitude, the cooling by radiation overnight is not too great. This result is a consequence of the small values of A_{21} and the ratio N/X .[*] For high altitudes where the relative concentration of oxygen atoms becomes greater (i.e., larger μ in equation (36)), the effect of radiative cooling due to the transition in the ^3P of the oxygen atom is somewhat greater.

The above result is obtained without considering the effect of the imprisonment of the radiation. It is clear that taking this into account will decrease the rate of cooling. In the particular problem of the atmosphere discussed above, this effect can be expected to be small. But in similar problems where the transition probability A is large, it is necessary to work with the equations (29) and (30).

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[*] In fact, for this and lower altitudes, a good approximation to the result of the preceding section could have been obtained directly from the ratio of the energy radiation for unit volume of the gas in 10 hours (calculated on the assumption of a Boltzmann distribution at the initial temperature) and the thermal energy density of the gas. For the constants in (43), this comes out to be 0.55 per cent, leading to a fall of 16° in temperature, instead of the 12° in Table I.

TABLE I

Nocturnal Cooling

(a) The radiative transition probability A_{21} for different values of the cross-section σ and the parameter λ . (N.B.: $A_{21} = 4.10^{-5}$ sec^{-1} is a reasonable value (Pasternack)[2])

$\downarrow \sigma$ (cm^2) \ $\overrightarrow{\lambda}$	1	10^{-3}	10^{-5}	10^{-7}	
10^{-16}	400	0.4	4.10^{-3}	4.10^{-5}	(sec^{-1})
10^{-18}	4	4.10^{-3}	4.10^{-5}	4.10^{-7}	
10^{-20}	.04	4.10^{-5}	4.10^{-7}	4.10^{-9}	

(b) The overnight drop in temperature. The temperature listed as a function of σ and λ is the temperature after 10 hours of radiative cooling, starting from an initial temperature $T_o = 300^oK$. See also Fig. 1

$\downarrow \sigma$ (cm^2) \ $\lambda \rightarrow$	1	10^{-3}	10^{-5}	10^{-7}	
10^{-16}	(7.4)	12	27	288	(^{o}K)
10^{-18}	9.9	27	288	299.9	
10^{-20}	16	288	299.9	300	

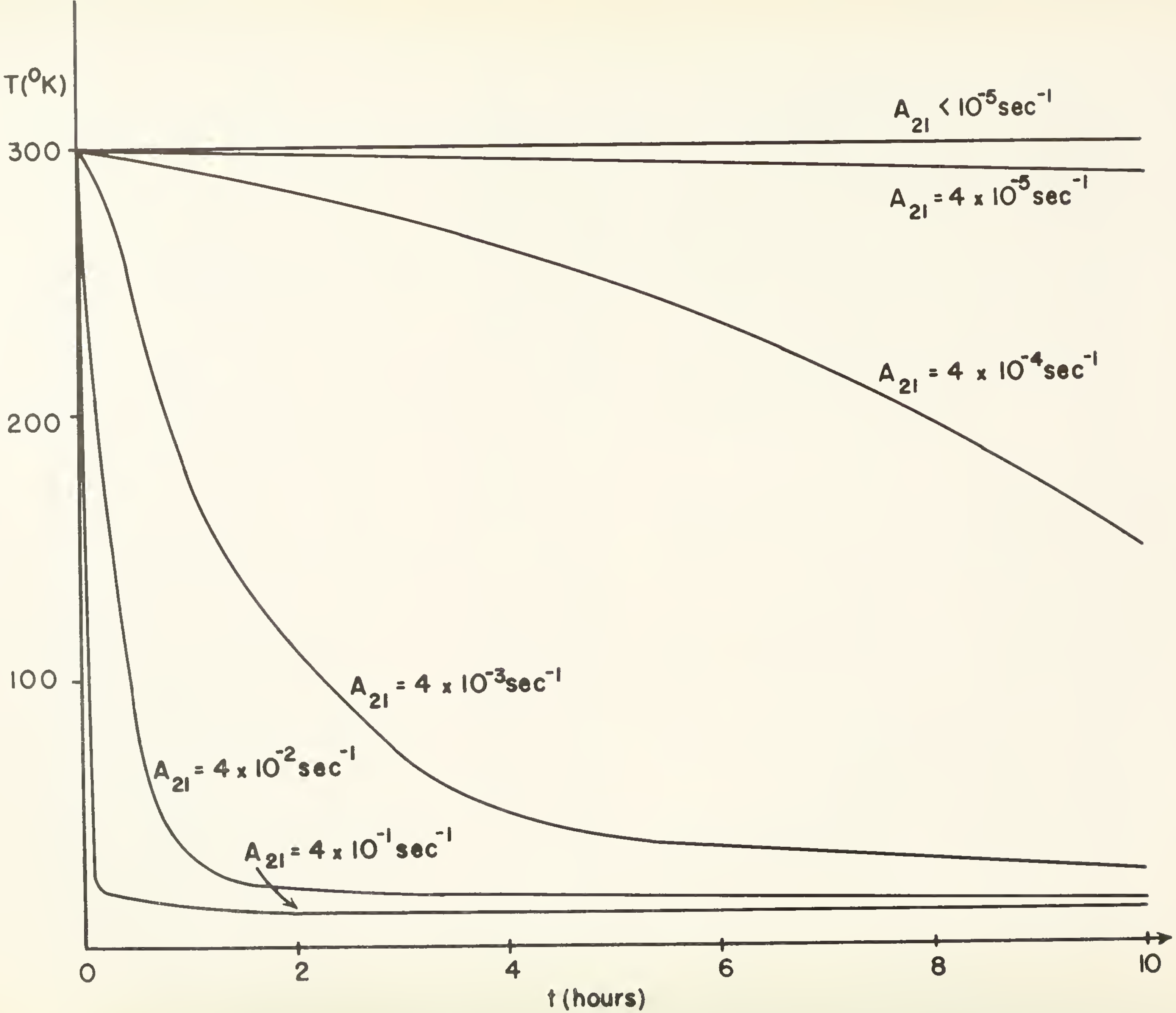

Figure 1. Nocturnal Cooling: Final Temperature: Starting from an initial temperature of 300°K, the temperature is given as a function of time for various values of the Einstein coefficient A_{21}. See also Table 1.

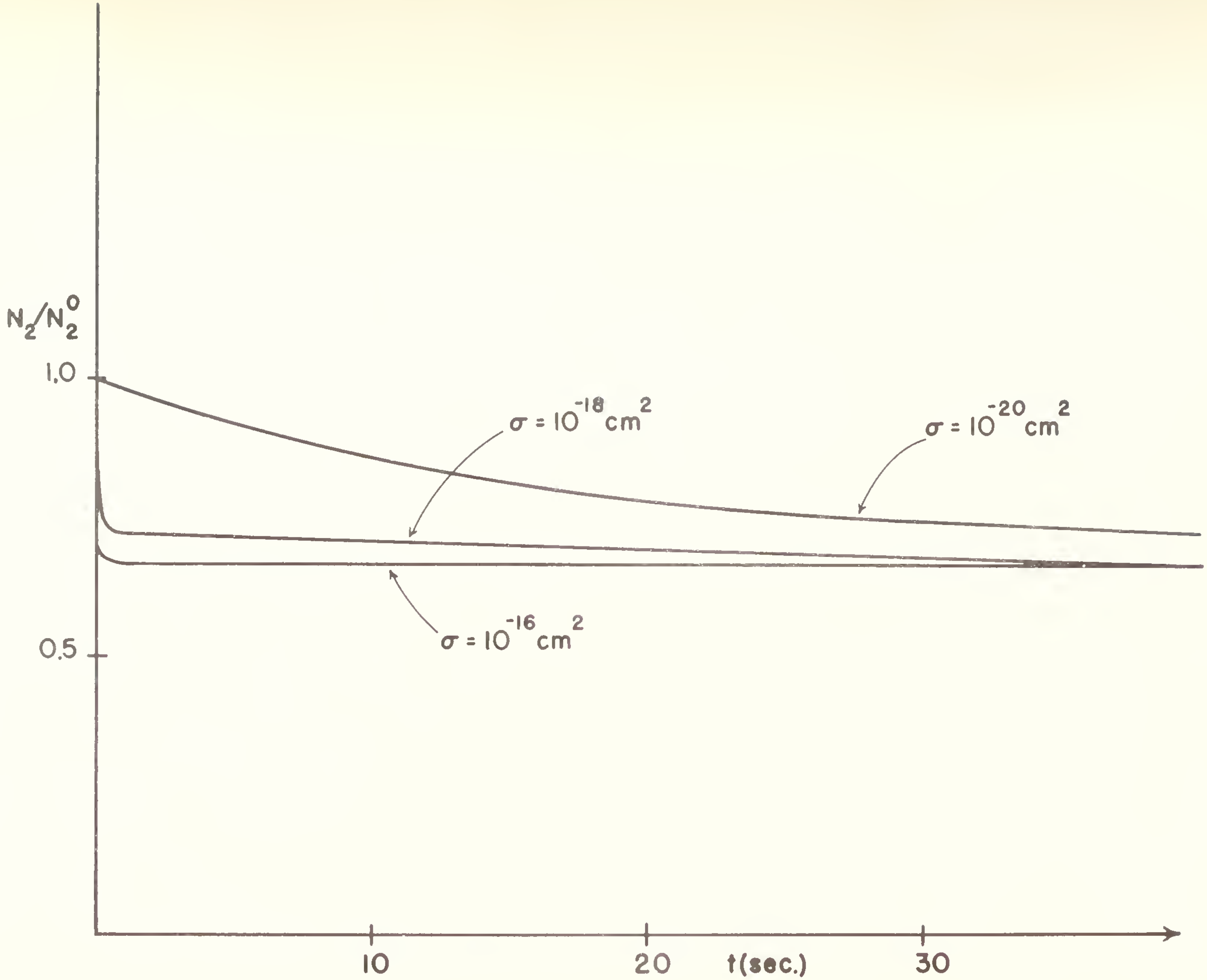

Figure 2. Disturbance of the Equilibrium Occupation Numbers due to Radiative Processes: The ratio N_2/N_2^0 of the actual occupation number N_2 of the excited state 2, to that predicted from the Boltzmann theorem for the appropriate temperature (N_2^0) is listed as a function of time, for the case $\lambda = 1$, for a number of values of the cross section σ and hence of the Einstein coefficient A_{21}.

Appendix. The numerical integration of equation (41).

We wish to integrate the equation

$$y \frac{dy}{dx} + J(x).y - K(x) = 0$$

$$x^2 J(x) = \lambda + g + e^{-x} + \frac{\mu g.x^2}{1+g.e^x} \tag{41}$$

$$x^2.K(x) = \lambda\mu.e^{-x}$$

with the initial condition

$$y = 0 \quad \text{at} \quad x = x_o = \frac{1}{2} \ . \tag{42}$$

The numerical integration proper is done in three parts for three different regions (i), (ii), (iii), described below.

Region (i): x just above x_o .

At $x = x_o$, $y = 0$, so that sufficiently close to z_o, (41) becomes

$$y \frac{dy}{dx} = K(x_o), \tag{A.1}$$

which is integrated by quadrature to give

$$\frac{y^2}{2} = K(x_o).(x - x_o) \qquad \text{for } y \ll K(x_o)/J(x_o). \tag{A.2}$$

Region (ii): from region (i) up to the maximum $y_1 = y(x_1)$.

Here we simply carry out a straightforward numerical integration.

Region (iii): $x > x_1$.

Here dy/dx is negative but very small compared to K/y or J, and thus y(x) is rather close to a function

$$\eta(x) = K(x)/J(x) \quad , \qquad (A.3)$$

which is the solution of an equation obtained from (41) by deleting the term y.dy/dx*,†.

The functions y(x) and $\eta(x)$ are related by the following important relations:

$$dy/dx \geq 0 \quad \text{if and only if} \quad y \leq \eta \qquad (A.4)$$

$$dy/dx \leq 0 \quad \text{if and only if} \quad y \geq \eta \; .$$

The actual numerical integration in range (iii) presents some technical difficulties because the derivative dy/dx is the small difference of the two relatively large quantities K/y and J. In trying to carry out the integration one observes empirically that errors build up very rapidly,

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[*] Note that $d\eta(x)/dx < 0$, and that its value is small compared with K/η or J(x).

[†] The purpose of the remainder of this discussion is to estimate the maximum error resulting from a replacement of y(x) by $\eta(x)$ for $x > x_1$. It is shown that for the values of the parameters used here, the maximum error nowhere exceeds 30 %, and thus does not affect the general order of magnitude of the results, which is all that is in question here. In fact, we see from Table II that for $\lambda = 10^{-5}$ the error is everywhere less than 1 %.

because the derivative is the difference of two large numbers whose first four significant figures (say) cancel. Furthermore, the solution obtained numerically oscillates with increasing amplitude about its mean value as errors build up. The standard method of dealing with this difficulty is to use a large number of significant figures and also to carry out evaluations at extremely small intervals in the independent variable x. This method is not practicable here, because the calculation becomes entirely too lengthy.

The procedure adopted here is to work with extremely large intervals, h, in x (" large" in a sense to be described below), and to furnish upper and lower bounds for the solution $y(x)$ for $x > x_1$. We now give the four steps in this procedure.

1) The function η (x) gives a lower bound for y(x) for $x > x_1$.

The y - and η- curves cross at $x = x_1$, where $\frac{dy}{dx} = 0$. For $x > x_1$, $y > \eta > 0$; hence $\frac{dy}{dx} < 0$, from equation (A.4); and no further crossing of the y - and η- curves is possible for $x > x_1$, because $\frac{dy}{dx} < 0$.

2) The dependence of oscillations in the solution y(x) on the interval h.

Consider points (x_n, y_n, η_n) and $(x_{n+1} = x_n + h, y_{n+1}, \eta_{n+1})$.

We ask: What is the condition that must be imposed on h in order that

$$y_{n+1} < \eta_{n+1} \quad \text{if} \quad y_n > \eta_n . \tag{A.5}$$

From (41) we have

$$(d/dx)y_n = K_n/y_n - J_n, \tag{A.6}$$

so that

$$y_{n+1} = y_n - h\,(J_n - \frac{K_n}{y_n}). \tag{A.7}$$

Then (A.5) will follow from (A.7) if the condition

$$\frac{\partial(y_{n+1} - \eta_{n+1})}{\partial(y_n - \eta_n)} < 0 \tag{A.8a}$$

is satisfied; and this is indeed the case if

$$h > y_n^2/K_n . \tag{A.8b}$$

Thus we see that oscillations in the integration occur for h larger than the critical size of equation (A.8b). We see from Table II that this critical size is quite small, so that it is not feasible to try to avoid the oscillations by using a sufficiently small value of h , since we have to carry out the integration over an infinite range of x .

3) An upper bound for $y(x)$ determined by a point-by-point method: given η_{n+1}, to find an upper bound for y_n .

From 2) above, we infer that when h is sufficiently large, then the value of $(y_n - \eta_n)$ will increase as the value of $(\eta_{n+1} - y_{n+1})$ increases.

Now, let the correct solution of (41) be $y(x)$. From 1) above, we know that $y_n > \eta_n$. Hence we may define a solution $z(x)$ of (A.7) such that $z_n > \eta_n$, $z_{n+1} = \eta_{n+1}$; and now we know that

$$\eta_n < y_n < z_n \quad . \tag{A.9}$$

Further, we know from (A.7) that z_n is given by the expression

$$z_n = \frac{1}{2}\left\{ \eta_{n+1} + h.J_n + \sqrt{(\eta_{n+1} + h.J_n)^2 - 4.h.K_n} \right\} . \tag{A.7'}$$

It must be stressed again that (A.9), (A.7') hold only for h such that equation (A.8b) is satisfied. Numerical values of h, η, z for typical x-values are listed in Table II, for $\lambda = 1$ and $\lambda = 10^{-5}$.

4) An upper bound for y(x) by a step-by-step method of integration.

The following method is recursive, rapid, and gives an adequate numerical upper bound for $y(x)$ in the present problem. It is a modified stepwise integration of equation (41) with an interval h larger than the minimum set by equation (A.8b)*.

Consider two points (x_n, y_n, η_n) and $(x_{n+1}, y_{n+1}, \eta_{n+1})$ satisfying equation (A.5). Now replace y_{n+1} by $y_{n+1}^{(1/2)}$, where

$$y_{n+1}^{(1/2)} = y_n - \frac{h}{2}\left[J_n - \frac{K_n}{y_n}\right] . \tag{A.10}$$

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* If h is smaller than the critical value, this method reduces to the usual one given in 2) above.

If $y^{(1/2)}_{n+1} > \eta_{n+1}$, we may substitute it, in turn, in (A.10), and obtain

$$y^{(1/2)}_{n+2} = y^{(1/2)}_{n+1} - \frac{h}{2}\left[J_{n+1} - \frac{K_{n+1}}{y^{(1/2)}_{n+1}}\right]. \qquad (A.10')$$

This process may be repeated until we reach some point x_m where $y^{(1/2)}_{m+1} < \eta_{m+1}$ while $y^{(1/2)}_{m} > \eta_{m}$. At this point, we continue as follows:

$$y^{(1/4)}_{m+1} = y^{(1/2)}_{m} - \frac{h}{4}\left[J_{m} - \frac{K_{m}}{y^{(1/2)}_{m}}\right] \qquad (A.11)$$

$$y^{(1/4)}_{m+2} = y^{(1/4)}_{m+1} - \frac{h}{4}\left[J_{m+1} - \frac{K_{m+1}}{y^{(1/4)}_{m+1}}\right], \qquad (A.11')$$

and so on (eventually we introduce $y^{(1/8)}$, $y^{(1/16)}$, ...).

This procedure works quite well in the present problem: it gives and upper bound because the absolute magnitude of the effective derivative decreases continually in this procedure; that is to say, in (A.10'), (A.11') we always have

$$y^{(1/2)}_{n+2} > \eta_{n+2}, \text{ whereas } y^{(*1/2)}_{n+2} = y^{(1/2)}_{n+1} - h\left[J_{n+1} - \frac{K_{n+1}}{y^{(1/2)}_{n+1}}\right] < \eta_{n+2}, \qquad (A.10'')$$

and

$$y^{(1/4)}_{m+2} > \eta_{m+2}, \text{ but } y^{(*1/4)}_{m+2} = y^{(1/4)}_{m+1} - \frac{h}{2}\left[J_{m+1} - \frac{K_{m+1}}{y^{(1/4)}_{m+1}}\right] < \eta_{m+2}. \qquad (A.11'')$$

Furthermore, in the present problem this method gives a rather smoothly varying function $y = y(x)$.

From the arguments 1) to 3) above it is clear that the method 4) does in fact give an upper bound to $y(x)$. In practice we see from Table II that it gives a better bound for $\lambda = 1$ than does the method 3), although in the case $\lambda = 10^{-5}$ the method 3) gives a better (i.e. lower) bound. There is of course no inconsistency in this.

$y(x)$ is given as a function of x in Fig. 3 for $\lambda = 1$ and 10^{-5} Beyond the maximum, we give a curve fitted smoothly to $\eta(x)$.

Table II: solution of equation (41) in region (iii), beyond the maximum.

		I		II	III
	x	h	$\eta(x)$	$\left(\frac{z-\eta}{\eta}\right)$ (%)	$\frac{y^{(1/2^n)}-\eta}{\eta}$ (%)
$\lambda = 1$	0.6	$3.6\text{x}10^{-3}$	.0383	0.4	0.49
	1.0	$6.8\text{x}10^{-3}$	.0267	26.8	0.86
	2.0	$10.2\text{x}10^{-3}$	.0104	9.6	7.5
$\lambda = 10^{-5}$	0.6	$0.68\text{x}10^{-7}$	$5.30\text{x}10^{-7}$	3.1	.01
	1.0	$1.28\text{x}10^{-7}$	$3.76\text{x}10^{-7}$	1	0.1
	2.0	$1.94\text{x}10^{-7}$	$1.50\text{x}10^{-7}$	1	0.1

In Column I, h is the minimum value permitted by equation (A.8b).
In Column II, $z(x)$ is the upper bound for $y(x)$ given by the point-by-point method of the appendix, paragraph 3).
In Column III, $y^{(1/2^n)}(x)$ is the upper bound of $y(x)$ given by the stepwise integration of the Appendix, paragraph 4).

Note how the errors in III accumulate with increasing x.

For $\lambda = 10^{-5}$, the method of paragraph 4) of the Appendix has been refined by using not $\frac{1}{2}$ dy/dx, but instead (1/p)dy/dx, where p is chosen such that $y_{n+1}^{(p)}$ is as small as possible but still satisfies the condition

$$\left| \frac{1}{p} \frac{d}{dx} y_n \right| < \left| \frac{d}{dx} y_{n+1}^{(p)} \right| ,$$

which is necessary for $y^{(p)}$ to remain an upper bound for $y(x)$.

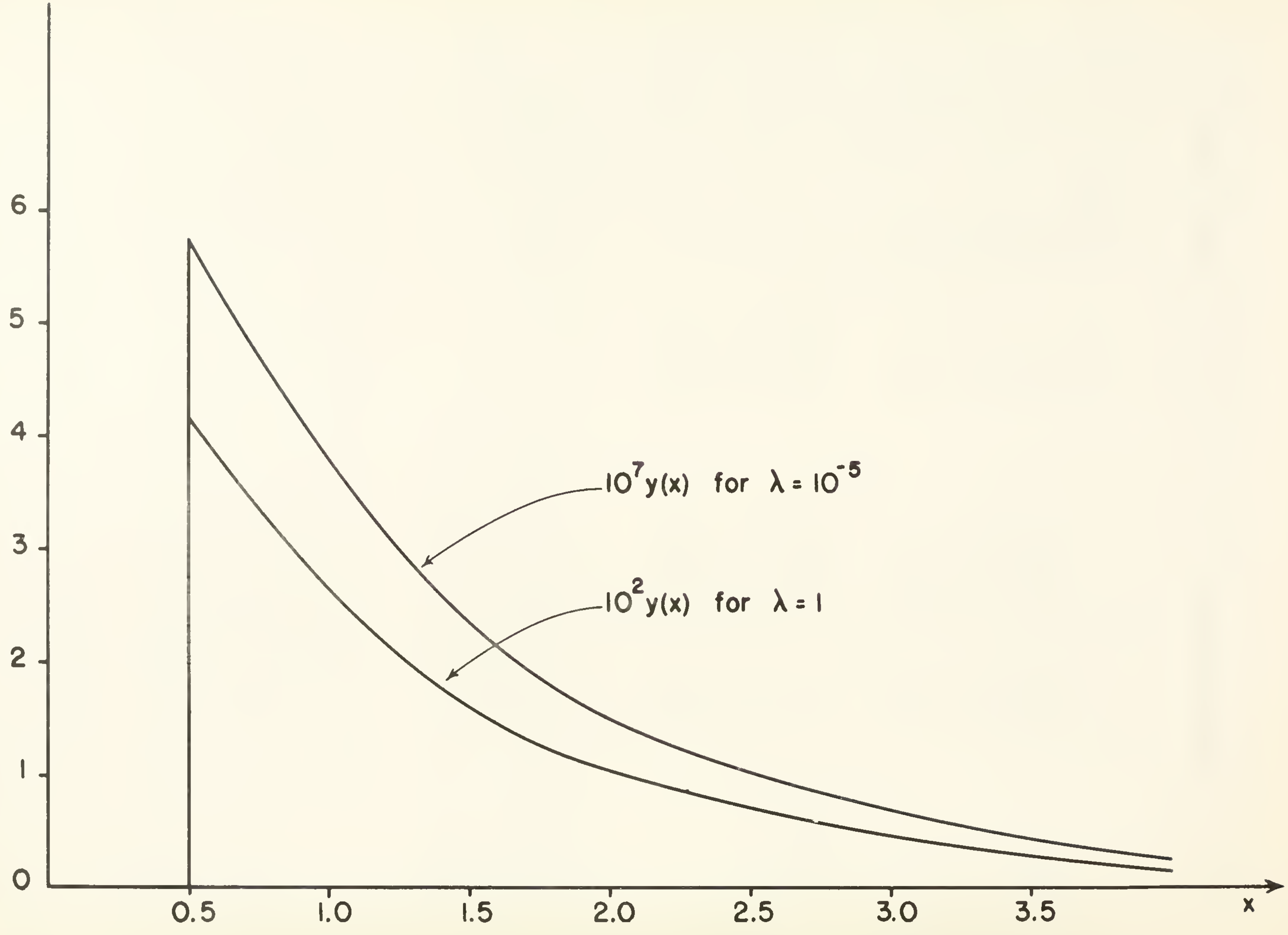

Fig. 3a The function $y(x)$ for $\lambda = 1$ and $\lambda = 10^{-5}$

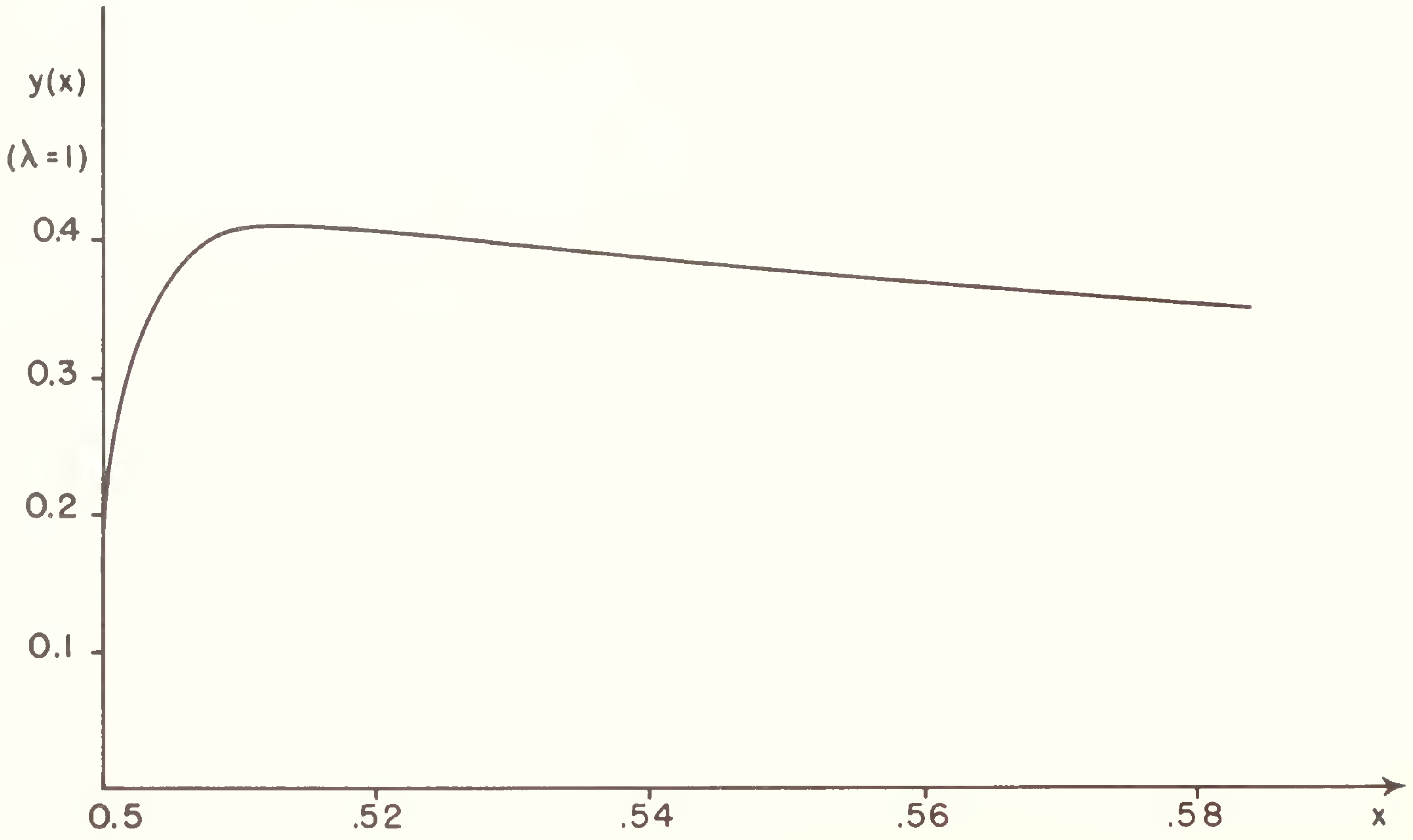

Fig. 3b   The approach to the maximum of $y(x)$ for $\lambda = 1$.

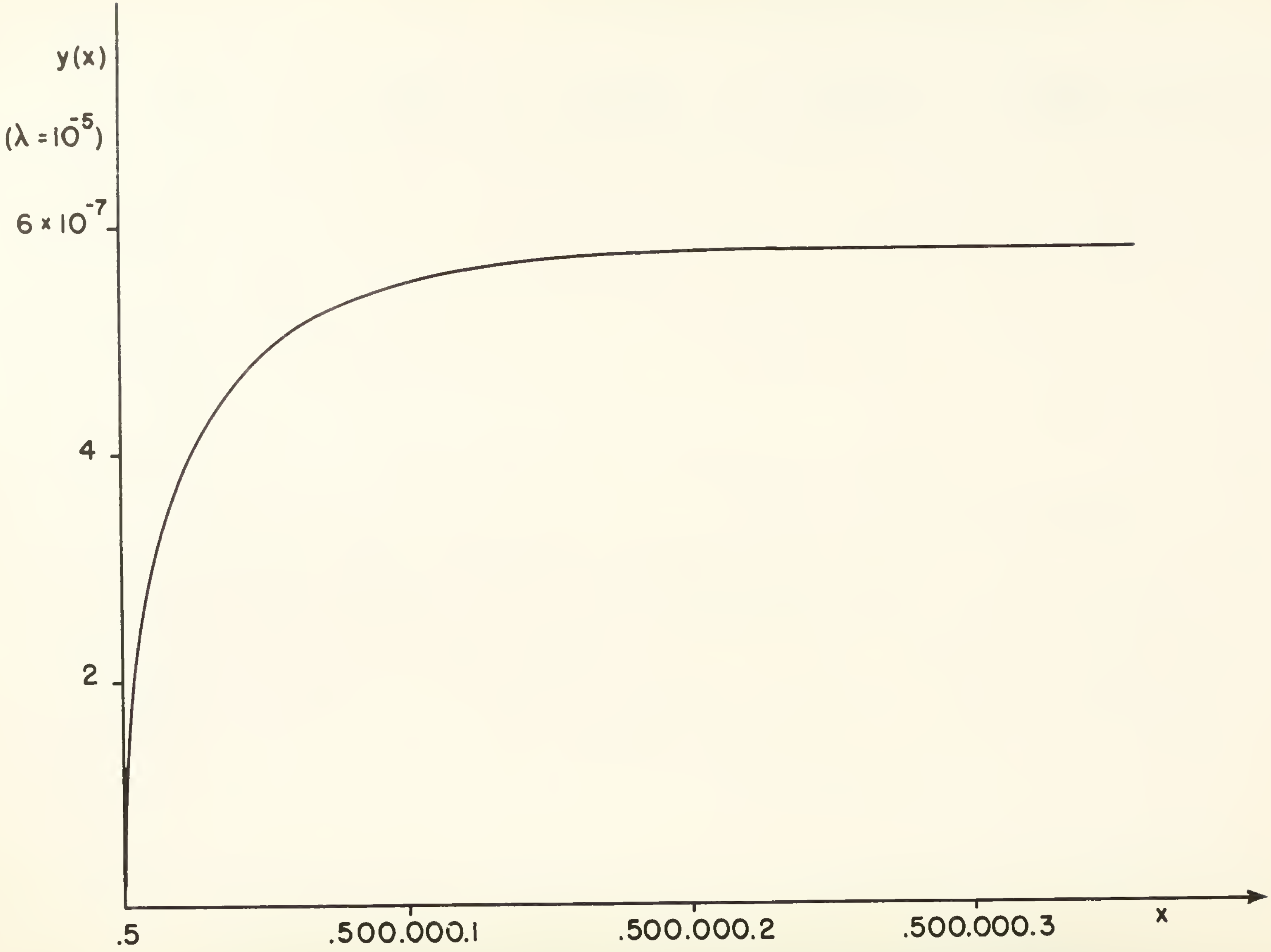

Fig. 3c The approach to the maximum of $y(x)$ for $\lambda = 10^{-5}$.

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